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A GENERALISED DIRECT EXCHANGE INTERACTION: APPLICATION TO HEUSLER ALLOYS

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ABSTRACT· A generalised Heisenberg-type exchange interaction is discussed. This arises from a combination of s–d mixing effects as well as s–d exchange. It is shown that the effective coupling shows an oscillatory behaviour. This mechanism is applicable to magnetic alloys where paramagnetic atoms are far separated from each other. A qualitative comparison with some Heusler alloys is made.

INTRODUCTION

In magnetically ordered solids where the paramagnetic ions are far separated from each other, the direct exchange interaction between their localised magnetic carriers is extremely feeble to bring about any appreciable coupling. One usually invokes mechanisms such as superexchange or indirect exchange, involving the role of the diamagnetic ions in magnetic compounds (Anderson, 1959; Kondo, Sinha and Tanabe, 1959). In magnetic metals and alloys the indirect exchange via the polarisation of conduction electron is often treated as the important mechanism. This is essentially a second order process involving s–d exchanges mechanism (Kasuya, 1956). The magnitude of this indirect exchange interaction decreases as the inverse third power of the distance between the magnetic ions in question (Ruderman and Kittel, 1954, Yoshida, 1957). However the sign of the interaction depends on the functions $F(x) = (x \cos x - \sin x)/x^4$ where $x = 2k_F R_{lm}$, k_F is the magnitude of the Fermi wave vector of conduction electrons and R_{lm} is the distance between the magnetic ion at R_l and R_m. In effect this gives a sort of oscillating behaviour with distance.

In the present paper we intend to generalise the direct exchange interaction by including s–d mixing effect as distinct from pure s–d exchange. We shall see that it incorporates both the effect of s–d exchange and s–d mixing. The s–d mixing is one electron effect and emanates from crystal field effects which can cause mixing of s and d orbitals on the same atom (intra-atomic mixing, Sinha and Upadhyaya, 1964), or between two different atoms (inter-atomic mixing, Anderson, 1961). The former will be present if the local symmetry at the site of the magnetic atoms is such that the crystal field has the appropriate

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symmetry to admix s and d states The latter is present even in ideally cubic crystal and connects s and d states on neighbouring atoms Owing to these effects, we cannot talk in terms of pure d and pure s orbitals The mixing effects ought to be taken into account in the description of the magnetic coupling.

In what follows, we formulate Heisenberg-like direct exchange interaction by taking cognizance of the mixing effects mentioned above. For its application we have in view Heusler alloys Cu_2MnX, where X may be Al, In, Sn, Ge, Sb, etc. Other types of exchange interactions involving this type of mixing for magnetically dilute alloys have been considered by a few workers (Kim and Nagaoka 1963; Alexander and Anderson 1964, see also Moriya 1965).

It will be shown that like the Ruderman-Kittel mechanism here also one gets some sort of oscillating behaviour

FORMULATION OF GENERALISED DIRECT EXCHANGE

Let us consider a magnetic crystal e.g Cu_2MnX which has paramagnetic ions far separated from each other along with other-nonmagnetic atoms The magnetic atoms have unpaired electrons in the d or f like orbitals unfilled shells. The non magnetic as well as the magnetic atoms contribute s like electrons which are in the conduction band in the system. Thus the total Hamiltonian for the d(localised) and conduction electrons can be expressed as

$$H = \sum_i H^{(1)}_{od} + \sum_j H^{(1)}_{os} + H_{sd} + \sum_{l<u} H_{lm} + H' \qquad (1)$$

where H' contains the Zeeman, lattice and electron-lattice parts of the Hamiltonian and will not be considered in the present formulation. $\sum_{l<m} H_{lml}$ are the two particle interaction terms and are responsible for $d-d$ and $s-d$ exchange process H_{sd} is the one electron interaction term which may arise due to local distortion at atomic site or crystal field effect of the neighbouring atoms in the undistorted situation. We will see that they will lead to mixing of s and d orbital states We will exploit these terms as perturbations over pure d and s states The pure d and s states are the solutions of the one electron Hamiltonians H_{0d} and H_{os} more more explicitly

$$H_{od}\,\phi_{dl} = E_{0l}\,\phi_{dl} \qquad \ldots (2)$$

$$H_{os}\,\phi_k = E_k\,\phi_k \qquad \ldots (3)$$

Here, ϕ_{dl} represents the localised d function in the field of atom at site R_l. ϕ_k is Bloch function for the band. We shall represent this as

$$\phi_k = \frac{1}{\sqrt{V}}\,u_k\,(r)\,e^{ik.r} \qquad (4)$$

For present purposes we consider a cubic crystal i.e. the field at the magnetic atoms has cubic symmetry. Thus the $s-d$ mixing for this case is confined to inter-atomic processes. The d orbital of atom at R_l is mixed with the s orbital at site R_m. We represent the solution of th reduced one electron Hamiltonian

$$(H^{(1)}{}_{0d}+H_{sd})\psi_l = E_l \psi_l \qquad \ldots (5)$$

where

$$\psi_l = \phi_{dl} + \sum_k e^{ik\cdot R_l} t_{kdl} \phi_k \qquad \ldots (6)$$

$$t_{kdl} = \frac{1}{\sqrt{N}} \frac{V_{kdl}}{\Delta E_{kd}} = \frac{1}{\sqrt{N}} \frac{\langle \phi_k | H_{II\text{-}F} e^{-ik\cdot R^l} | \phi_{dl} \rangle}{\Delta E_{kd}}$$

Likewise, the conduction electron wave function is also modified from ϕ_k owing to this interaction. They can be designated by

$$\psi_k = \phi_k - \sum_l e^{-ik} R_l t_{dlk} \phi_{dl}$$

which are nearly orthogonal to ψ_l. However, we shall not require these explicitly in the present formulation.

Let us now evaluate the two particle exchange interactions in terms of the localised states given by ψ_l etc. In doing so we make use of the second quantized representation (Landau and Lifshitz, 1958) We make use of the particle field operators.

$$\chi(\xi) = \sum_{j\sigma} \psi_{\sigma i} C_{i\sigma}, \chi^+(\xi) = \sum_{i\sigma} \psi^+{}_{i\sigma} C^+{}_{i\sigma} \qquad \ldots (7)$$

The two particle interaction is then given as

$$\int \chi^+(\xi) \chi^+(\xi') \left(\sum_{l<m} H_{lm}\right) \chi(\xi) \chi(\xi') d\xi d\xi^1$$

Making use of the operator (7), this is written as

$$\sum_{l<m} C^+{}_{l\sigma} C^+{}_{m\sigma^1} < \psi_{l\sigma} \psi_{m\sigma^1} | H_{12} | \psi_{m\sigma} \psi_{l\sigma'} > C_{m\sigma} C_{(\sigma)} \qquad \ldots (8)$$

In these expressions $C^+{}_{i\sigma}$, $C_{i\sigma}$ etc. are the fermion creation and annihilation operators with respect to states $\psi^+{}_{i\sigma}$ and $\psi_{i\sigma}$ respectively: σ is the spin index.

We now re-express the matrix elements in (8) invlving $\psi_{i\sigma}$ and $\psi_{m\sigma^1}$ etc. in terms of the explicit expressions like (6).

The expanded form will contain sixteen terms. However, this can be reduced on the basis of the following arguments. We select ϕ_l and ϕ_m as extremely localised functions and hence their overlap is negligible. Thus those matrix elements which involve pure $\phi_l(1)$ $\phi_m(1)$ as factors will be neglected. This rules out all the first and second order terms. In the third order terms the strongest will be those which involve intra-atomic exchange along with the transfer processes.

Processes other than this and of higher order in perturbation are neglected. Thus, we concentrate on the processes such as

$$\frac{2\Sigma}{l,m}\sum_{kk'}\sum_{\sigma\sigma'} t_{dlk'}\,\langle\phi_k\phi_m|H_{12}|\phi_m\phi_k\rangle\, t_{kdl}C^{+}_{l\sigma}C^{+}_{m\sigma'}C_{m\sigma}C_{l\sigma} \qquad \ldots\ (9)$$

Let us carry out the summation over the spin indices, and write the above expression in terms of the spin operators For this we have to utilise the relations (Sinha and Upadhyaya 1962),

$$\begin{aligned}
&C^{+}_{l(+)}C_{l(-)} = S_{lx}+iS_{ly}\\
&C^{+}_{l(-)}C_{l(+)} = S_{lx}-iS_{ly}\\
&C^{+}_{l(+)}C_{l(+)}-C^{+}_{l(-)}C_{l(-)} = 2S_{lz}\\
&C^{+}_{l(+)}C_{l(+)}+C^{+}_{l(-)}C_{l(-)} = 1
\end{aligned} \qquad \ldots\ (10)$$

The equation (9) then reduces to

$$-\frac{2\Sigma}{lm,kk'}\sum_{\sigma}^{\prime} e^{ik,R_l}\, t_{dlk}\,\langle\phi_k\phi_m|H_{12}|\phi_m\phi_k\rangle t_{kdl}e^{-ik,R_l}\times\tfrac{1}{2}(1+4S_l\ S_m) \qquad \ldots\ (11)$$

where S_l, S_m are the vector spin operators of an electron associated with states ψ_l, ψ_m etc. We now concentrate on summation over k and k' and it would therefore suffice to consider the matrix elements,

$$\sum_{k}\sum_{k'} e^{ik'R_l}t_{dl,k'}\,\langle\phi_{k'}\phi_{dm}|H_{12}|\phi_{d_m}\phi_k\rangle\, t_{k,dl}e^{-ik\,.\,R_l}$$

$$=\frac{1}{N^2}\sum_{k,k'} e^{ik'\,.\,R_l}\left(\frac{V_{dl,k'}}{\Delta Ek\,d}\right)J(k-k')\,e^{\,i(k-k')\,.\,R_m}\left(\frac{V_{kdl}}{\Delta E_{kd}}\right)e^{-ik\,.\,R_l} \qquad \ldots\ (12)$$

where

$$J\,(k-k') = N\int e^{-i(k-k')\,.\,R_m}\,\frac{\phi^{*}k'(r_1)\phi^{*}_{dm}(r_2-R_m)e^2\phi_k(r_1-(r_2)R_,)\phi_{dm}\;d\tau_1 d\tau_2}{r_{12}} \qquad \ldots\ (13)$$

As done by others (Yosida, 1957), we shall assume that $J(k-k')$ does not depend strongly on k and k'. It is customary to replace this by the intra-atomic s - d exchange integral which gives the maximum contribution at one site. The denominators in (12) are of the form

$$\Delta E_{kd} = E_k - E_d = \frac{\hbar^2k^2}{2m^*} - E_l \equiv \frac{\hbar^2}{2m^*}\,(k^2+a^2) \qquad \ldots\ (14)$$

where $\hbar^2k^2/2m^*$ is the energy of the conduction electron in state k, E_d is that which corresponds to localised pure d states; and $a^2 = (2m/\hbar^2)\Delta$ where Δ is the energy gap between the bound d-state and the bottom of the conduction band.

Thus the integral in (12) reduces to

$$\frac{1}{N^2}\sum_{kk'}\frac{V_{dl,k'}J(k'\quad k)\,V_{kdl'}e^{-i(k-k').(R_l-R_m)}}{(\hbar^4/(2m^*)^2)(k^2+a^2)(k'^2+a^2)} \qquad (15)$$

Next, we change from summation to integration, we get

$$\frac{1}{N_2}\quad\frac{(V_{sd})^2}{\hbar^4/(2m^*)}\quad\frac{V^2}{8\pi^3}\int_0^{k_F}\int_{k_F}^{\infty}\frac{e^{-i(k-k').R_{lm}}}{(k^2+a^2)(k'^2+a^2)}d^3k\,d^3k' \qquad (16)$$

In putting the limits of integration, we are guided by the exclusion principle; k_F is the wave-vector at the Fermi surface. This is evaluated below. We do not make any approximation regarding k^2+a^2 and k'^2+a^2. The value of the integral is then

$$16\pi^2k_F^2\left[\frac{\pi}{2}e^{-\lambda x}\frac{\cos x}{x^3(1+\lambda^2)}-\frac{\cos^2 x}{x^4(1+\lambda^2)^2}-\frac{\pi}{2}e^{-\lambda x}\frac{\sin x}{x^4(1+\lambda^2)}\left(1-\frac{2}{1+\lambda^2}\right)+\ldots\right] \qquad \ldots\ (17)$$

where $$\lambda = \frac{a}{k_F} \quad \text{and} \quad x = k_FR$$

The final expression (cf. equation 17) is most general. One point which can be easily inferred from this is that the function is oscillating and changes sign periodically in a damped manner as a function of Rk_F.

The complete expression for the exchange interaction between the magnetic atoms is then given by (cf. equation (11))

$$-\sum_{(l,m)}\frac{V_{sd'}^2J_{sd}}{\hbar^4/(2m^*)^2}\frac{V^2}{N^2}\,16\pi^2k_F^2\left[\frac{\pi}{2}e^{-\lambda x}\frac{\cos x}{x^3(1+\lambda^2)}-\frac{\cos^2 x}{x^4(1+\lambda^2)^2}\right.$$

$$\left.-\frac{\pi}{2}e^{-\lambda x}\frac{\sin x}{x^4(1+\lambda^2)}\left(1-\frac{2}{1+\lambda^2}\right)+\ldots\right]S_l.\,S_m \qquad \ldots\ (18)$$

where the summation over l, m involves nearest neighbours only. The function given in the square bracket of (18) has been plotted in Fig.1, against the parameter Rk_F which involves the separation between magnetic atoms. We have shown the

various curves with different values of the gap parameter, namely, $(\lambda = (a/k_F)$. For comparison the Ruderman-Kittel $(R-K)$ function in the form

$$(2x \cos 2x - \sin 2x)/(2x)^4, \text{ where } x = k_F R,$$

has also been plotted It can be seen that for the initial values of the argument the two prediction differ, whereas R-K curve indicates ferromagnetic coupling

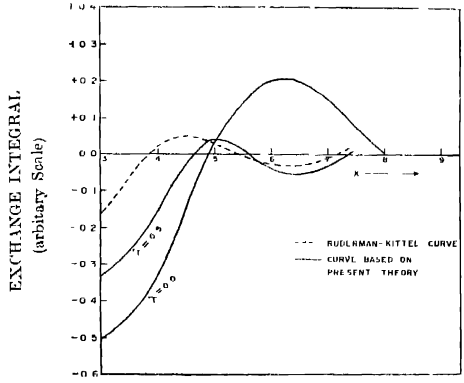

Fig. 1. Plot of exchange integral vs. X with λ as gap parameters

the present curve gives antiferromagbetic coupling. Later on the oscillation periods are similar However, the curve based on the present analysis is more flexible and the ferromagnetic and antiferromagnetic regions contract or expand depending on the gap parameter. This has been displayed clearly.

APPLICATION TO HEUSLER ALLOYS

For actual comparison with experimental results we select some magnetic alloys of the form Cu_2 Mn X with X standing for Al, Sn, In, Sb, etc This system in the ordered phase (which is of interest at present) has a body centred cubic structure with a face centredsuperstructure (Bradley and Rodgers, 1934) The copper atoms are at the cube corners and Mn and X alternate at the body centres. The magnetic moment is localised at the Mn atoms which are supposed to have four unpaired *d* electrons. As can be seen from the structure, there is no direct overlap between two Mn atoms owing to the presence of the intervening diamagnetic atoms. The distance between nearest Mn-Mn neighbour is about 4.2Å. We shall select the system Cu_2MnSb which is antiferromagnetic and for which some data have been reported by Oxley *et al* (1963). From their data the order of the parameter Rk_F turns out to be 4.35. This falls in the antiferomagnetic region in our graph whereas this corresponds to ferromagnetic region of

R-K curve. It may, however, be noted that the actual coupling will be due to the overall effective exchange i.e. arising from the R-K mechanism, generalised Heisenberg type interaction discussed here and other superexchange type processes. An exact comparison with experimental results with many systems does not seem to be possible owing to a lack of knowledge of k_1 and other parameters. We do not know as to how many conduction electrons per atom are to be taken for each system We must await some experimental work in this direction.

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